

CLAIMS

1. A method for preparing a conjugated molecule comprising a first monomer coupled to a second monomer, said method comprising:

5 (i) linking the first monomer to a solid support via the germanium atom of a germyl linking group;

(ii) coupling the first monomer to the second monomer in a coupling position to form a bound conjugated molecule, wherein the second monomer has a protecting group in a non-coupling position;

10 (iii) optionally sequentially coupling a third, fourth....and n^{th} monomer to the second, third and $(n-1)^{\text{th}}$ monomer respectively;

(iv) removing the protecting group; and

(v) *ipso*-degermylation to release the bound conjugated molecule.

15 2. A process for preparing a conjugated molecule comprising a first monomer coupled to a second monomer, said method comprising:

(A) linking the first monomer to a solid support via the germanium atom of a germyl linking group and, if necessary, activating a position on the first monomer

20 (B) coupling the first monomer to a second monomer in a coupling position to form a bound conjugated molecule, wherein the second monomer has a protecting group in a non-coupling position

(C) optionally removing the protecting group and repeating (B) with one or more further monomer molecules one or more times, optionally using monomer molecules without protecting groups or removing protecting groups as required if present

25 (D) if desired removing a protecting group if present; and

(E) *ipso*-degermylation to release the bound conjugated molecule.

30 3. A process according to claim 2 in which the coupling of (B) is repeated at least once to obtain a higher degree of conversion.

4. A process according to claim 1, 2 or 3 in which each of the monomers contributes to a π -system of the conjugated molecule.

35 5. A process according to any preceding claim in which each of the monomers is independently selected from the group consisting of aromatic carbocyclic monocyclic or polycyclic (eg fused polycyclic) monomers which are optionally ring substituted, unsaturated monocyclic or polycyclic (eg fused polycyclic) heterocyclic (eg heteroaromatic) monomers which are optionally ring substituted, and unsaturated acyclic hydrocarbon bridging monomers.

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6. A process according to claim 5 in which one or more of the monomers has a ring substituent which enhances properties, for example, the electronic properties, of the conjugated molecule.

7. A process according to any preceding claim in which the conjugated polymer is a polyheterocycle, wherein at least one of the monomers (preferably at least the first monomer) is ring substituted.

8. A process according to any of claims 5 to 7 in which at least one of the monomers is a 5- or 6-membered optionally ring substituted heterocyclic monomer unit which may contain one, two or three heterocyclic atoms which may be the same or different.

9. A process according to claim any of claims 5 to 8 in which the (or each) heterocyclic atom is selected from the group consisting of nitrogen, sulphur, oxygen, phosphorous and selenium.

10. A process according to any of claim 9 in which the (or each) heterocyclic atom is nitrogen or sulphur.

11. A process according to claim 1 to 4 in which at least one monomer group of formula $-Ar^iNAr^jAr^k-$ is present, the groups Ar^i , Ar^j and Ar^k being aryl groups, in which the aryl groups may be phenyl groups.

12. A process according to claim 11 in which Ar^k is substituted (eg *o*- or *p*-substituted) with a group which has an electron withdrawing or donating effect.

13. A process according to claim 11 in which Ar^k has a substituent which enhances the solubility of the conjugated compound in aromatic or chlorinated solvents.

14. A process according to any preceding claim in which at least one of the monomers is thiophene which may be substituted at the 3- or 4-position with an alkyl group (eg a C_{1-12} -alkyl such as a hexyl or octyl) or an aryl (eg a phenyl) group.

15. A process according to any preceding claim in which the protecting groups are silyl groups of formula $SiR^iR^jR^k$ in which R^i , R^j and R^k are independently alkyl groups having 1 to 4 carbon atoms or phenyl groups for example Me_3Si , Et_3Si , iPr_3Si , Me_2PhSi and preferably Me_2^tBuSi (TBDMS) or corresponding silyloxy groups.

16. A process according to claim 11 in which the silyl protecting group is removed in step (D) nucleophilically with a basic source (eg K_3PO_4 or Cs_2CO_3) and/or a fluoride source (eg CsF or nBu_4NF).

17. A process according to any preceding claim in which the *ipso*-degermylation of step (E) is an *ipso*-protodegermylation i.e. cleavage in which the germanium link is replaced by a proton.

18. A process according to any one of claims 1 to 17 in which an electrophilic *ipso*-degermylation (eg *ipso*-halodegermylation) is carried out..

19. A process according to claim 18 in which *ipso*-protodegermylation is carried out using a strong organic acid (for example trifluoroacetic acid (TFA), HCO_2H , $AcOH$, $ClCH_2CO_2H$ or Cl_2CHCO_2H), a mineral acid (for example HCl , H_2SO_4 or HF) or a source of fluoride ions (for example CsF or Bu_4NF).

20. A process according to claim 19 which is carried out under mild conditions whereby silyl groups are not removed.

21. A process according to claim 19 or 20 in which the electrophilic *ipso*-degermylation is carried out using a source of halonium ions (F^+ , Cl^+ , Br^+ or I^+), NO^+ , NO_2^+ , SO_3^+ , RCO^+ , RSO_2^+ , $BHal_2^+$ (eg BCl_2^+) or $B(OH)_2^+$.

22. A process according to any preceding claim in which degermylation is carried out under mild conditions whereby the protecting group is left intact to release a protected conjugated molecule.

23. A process according to claim 21 in which the protecting group is subsequently removed in step (D) using a different electrophile to produce an unsymmetrical conjugated molecule.

24. A process according to any preceding claim in which the protecting group is removed simultaneously with degermylation (eg electrophilic *ipso*-desilylation) releasing a symmetrically end functionalised conjugated molecule.

25. A process according to any preceding claim in which step (E) comprises: *ipso*-degermylation using an electrophilic group E to release the bound conjugated molecule with an end functionality E; and then reacting the conjugated molecule having end functionality E with a compound $A'Y'$ wherein group Y' is capable of displacing end functionality E.

26. A process according to claim 25 in which the end functionality E is bromine, iodine or a boronic group such as a boronic acid group or a derivative thereof (eg an ester derivative thereof) for example a boronic acid group of formula $-B(OR)_n$ (wherein: n is 2 or 3; and each R is independently hydrogen or an optionally substituted linear or branched C_{1-6} -alkyl group or two groups R represent an optionally substituted alkano bridging group between two oxygen atoms, for example, an optionally substituted ethano or propano bridging group).

27. A process according to claim 25 in which Group Y' is an end capping group for example a linear or branched alkyl (eg C_{1-6} -alkyl), aryl, benzyl, vinyl, propargyl, allyl or alkynyl group or a conjugated molecule such as an oligoheterocyclic group.

28. A process according to claim 25 or 27 in which Y' is a functionalised block conjugated polymer or oligomer group for example a block of thiophene or pyridine units and A' is bromine, iodine or an organometallic functionality for example an organomagnesium, organozinc or organotin functionality or preferably an organoboron functionality eg $B(OR')_n$, particularly preferably $B(OH)_2$ wherein: n is 2 or 3; and each R is independently hydrogen or an optionally substituted linear or branched C_{1-6} -alkyl group or two groups R represent an optionally substituted alkano bridging group between two oxygen atoms.

29. A process according to any preceding claim in which step (B) comprises halogenating the first monomer in a coupling position; and reacting the product with the second monomer metallated in a coupling position or metallating the first monomer in a coupling position; and reacting the product with the second monomer halogenated in a coupling position.

30. A process according to claim 29 in which the halogenation is carried out using bromine or iodine or a source thereof preferably 1,2-diiodoethane, optionally in the presence of a mercury salt such as acetate or hexanoate.

31. A process according to claim 29 or 30 in which the first or second monomer is metallated at its coupling position with a metallic group, for example selected from organoboron, organomagnesium, organotin and organozinc groups.

32. A process according to claim 31 in which the boronic group is a boronic ester group or preferably a hypervalent boronate complex.

33. A process according to claim 31 in which the boronic group is a boronic acid group or derivative thereof.

34. A process according to claim 31, 32 or 33 in which the boronic group is of formula:



wherein: n is 2 or 3; and each R^y is independently hydrogen or an optionally substituted linear or branched C₁₋₆-alkyl group or two groups R^y represent an optionally substituted alkano bridging group between two oxygen atoms.

35. A process according to claim 32 in which the hypervalent boronate complex is a hypervalent alkyl boronate complex with a suitable metal counterion (eg Na or (preferably) Li).

36. A process according to any preceding claim in which the first monomer is metallated (preferably lithiated) in the chosen position and reacted with an immobilised germyl linking group which has a suitable leaving group which is preferably chloride.

37. A process as claimed in any preceding claim in which one monomer is a compound of formula:



wherein: M is a counter ion; for example an alkali metal, for example Na or Li, X is an optionally ring substituted unsaturated monocyclic or polycyclic (eg a fused polycyclic) hydrocarbon or heterocyclic moiety which may be linked to the germanium atom; and each group R is independently hydrogen or an optionally substituted linear or branched C₁₋₆-alkyl group or two groups R represent an optionally substituted alkano bridging group between two oxygen atoms.

38. A process according to claim 37 in which the group X is a ring substituted heterocyclic moiety which may contain one, two or three heterocyclic atoms which may be the same or different and are preferably selected from the group consisting of nitrogen, sulphur, oxygen, phosphorous and selenium, preferably the group consisting of nitrogen, oxygen and sulphur, and more preferably the group consisting of nitrogen and sulphur.

39. A process according to claim 37 or 38 in which the heterocyclic moiety is a 5- or 6-membered optionally ring substituted heterocyclic moiety preferably selected from the

group consisting of optionally ring substituted thiophene, furan, pyridine, imidazole, isothiazole, isooxazole, pyran, pyrazine, pyridazine, pyrazole, pyridine, pyrimidine, triazole, oxadiazole, pyrrole, indazole, indole, indolizine, pyrrolizine, quinazoline, quinoline and phenyl.

40. A process according to claim 37, 38 or 39 in which the heterocyclic moiety is selected from the group consisting of optionally ring substituted thiophene and pyridine and preferably thiophene which may be substituted at the 3-position with an alkyl group (eg a C₁₋₈-alkyl such as a hexyl or octyl) or an aryl (eg a phenyl) group.

41. A solid support for carrying out a process as claimed in any preceding claim of formula X(OR^x-GeR¹R² Hal)_n in which X is a high molecular weight material of low solubility in water and organic solvents, suitably a hydrocarbon resin substituted by alkoxy chains, for example polystyrene substituted by alkoxy, preferably propoxy or more preferably ethoxy or propoxy/ethoxy chains, R^x is a hydrocarbon group suitably having 1 to 12 and more preferably 3 to 10 carbon atoms, for example an alkyl, aryl group or arylalkyl group, the aryl group suitably comprising a benzene ring optionally substituted by alkyl groups, the Ge being preferably linked to an alkyl group, R¹ and R² individually being alkyl or aryl groups for example phenyl or tolyl groups, preferably having 1 to 10 carbon atoms and Hal representing a halide for example a bromide, iodide or preferably chloride atom and n being a large integer.

42. A solid support as claimed in claim 41 in which R¹ and/or R² is an aryl group substituted by an electronegative group which advantageously improves the efficiency of subsequent germanium cleavage.

43. A solid support according to claim 42 in which the electronegative group is an alkoxy or halogen group wherein the alkoxy group contains 1 to 6 carbon atoms.

44. A process according to any of claims 1 to 40 in which the support is as claimed in any one of claims 41 to 43.